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Photopolymerization of methyl methacrylate and 2-(dimethylamino) ethyl methacrylate induced by diacetoxyiodobenzene in the presence of radical inhibitors

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Summary

Polyvalent iodine compounds such as diacetoxyiodobenzene, $(CH_3COO)_2IC_6H_5$ (DAI), and bis(trifluoroacetoxy)iodobenzene, $(CF_3COO)_2IC_6H_5$ (BTI), are efficient initiators of cationic and radical polymerizations. To confirm the radical mechanism of DAI-induced polymerization of methyl methacrylate (MMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA), a study has been performed in the presence of the radical inhibitor 2,3,5,6-tetrachloro-p-benzoquinone (TCQ) and its complex with triethylamine (TEA). The polymerization kinetics and the effect of irradiation intensity have been studied.

Introduction

Polyvalent iodine compounds are a very perspective new class of polymerization initiators. However, the initiation mechanism still remains scarcely investigated. The use of DAI and BTI as cationic photoinitiators has been reported (1). Later studies (2,3) have shown that these compounds may initiate the polymerization of monomers such as MMA and DMAEMA known to polymerize typically by radical mechanism. To prove this mechanism, DAI-photoinitiated polymerizations of MMA and DMAEMA have been carried out in the presence of 2,3,5,6-tetrachloro-p-benzoquinone (TCQ) and its complex with triethylamine (TEA) known as efficient radical inhibitors (4,5).

Experimental

MMA and DMAEMA were purified by distillation at reduced pressure. The initiator (DAI) was prepared using a standard method (6). Photopolymerizations were carried out in dichloromethane solution. Monomer and initiator concentrations were 3.5 and 0.015 mol/l, respectively. The samples were irradiated from a distance 10 cm by a 125 W medium pressure Hanovia mercury lamp at room temperature in air. For some experiments, the distance between the lamp and the sample was varied to ensure controlled irradiation intensity. TCQ purified by recrystallization, as well as its complex with TEA (used as received) were used as inhibitors. The polymers prepared were isolated by precipitation with petroleum ether (b.p.40-60°C) and dried to a constant weight at 70°C. The polymerization rate was determined gravimetrically.

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Results and discussion

1. The effect of monomer feed composition on the rate of photoinduced copolymerization of MMA and DMAEMA.

Fig.1 shows that MMA and DMAEMA copolymerization rate is unaffected by the feed composition at a constant molar monomer concentration. This has been attributed to the similar π-electron systems of both monomers. A slight difference in their reactivities might be expected because of a possible hydrophobic interaction between the dimethylaminoethyl groups of DMAEMA. However, all the polymerizations have been carried out in a weakly polar solvent, dichloromethane, where such an interaction is minimal, so that the same inhibiting effect of TCQ-TEA complex on the homopolymerization of MMA and DMAEMA is expected.

2. Inhibition of the photoinduced homopolymerization of MMA and DMAEMA by TCQ-TEA complex.

The influence of TCQ and TEA on MMA and DMAEMA homopolymerization rates has been investigated. The results are given in Table 1. Obviously, TEA does not affect the homopolymerization rates of either monomer. However, TCQ behaves in a quite different manner. While it somewhat slows down the MMA homopolymerization without any induction period, it stops the DMAEMA homopolymerization completely. However, when the TCQ amount was decreased to 6% mol of that of the initiator, DMAEMA polymerization proceeded with a rate of 6 %/h and 12 min induction. A 1:1 mole ratio of MMA and DMAEMA does not polymerize in the presence of TCQ (0.0072 mol/l). The great difference of TCQ inhibition on MMA and DMAEMA homopolymerization must be due to the formation of TCQ-DMAEMA complex:

$$\mathrm{TCQ} + \mathrm{DMAEMA} \rightleftharpoons [\mathrm{TCQ}^{-\cdot}, \mathrm{DMAEMA}^{+\cdot}] \qquad (1)$$

(DMAEMA is an n-electron donor similar in action to TEA.)

The large excess of DMAEMA in relation to TCQ ensures that all TCQ is complexed, and the complex strongly inhibits the radical polymerization of DMAEMA. It is now clear why TCQ alone does not inhibit the polymerization of MMA, whereas efficient

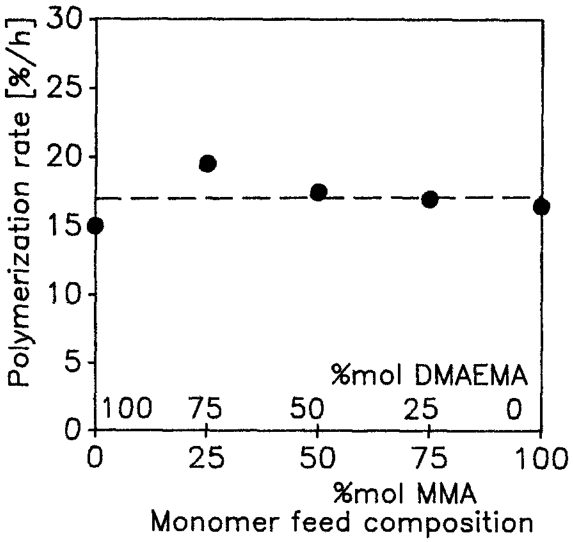

Fig.1. The dependence of the copolymerization rate of MMA and DMAEMA on the monomer feed composition

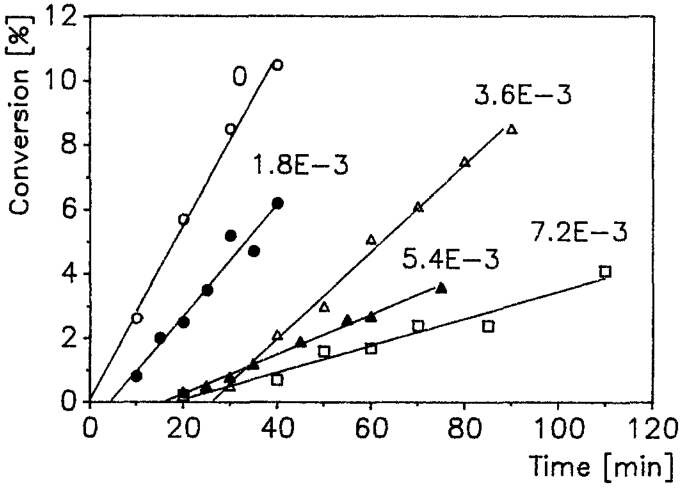

Fig.2. TCC-TEA complex effect on MMA polymerization kinetics. The molar concentrations of the inhibitor are given on the figure.

inhibition occurs with a tertiary amine, as shown by the data in Fig.2. MMA polymerization is inhibited by the TCQ-TEA complex and the polymerization rate decreases after an induction period with the increase of the inhibitor concentration. Fig.3 shows the effect of inhibitor concentration on the polymerization rate and induction time. Possibly the inhibiting system retards the polymerization under these conditions.

These results demonstrate that a radical mechanism is responsible for the DAI-photoinduced polymerization of MMA and DMAEMA.

3. The effect of irradiation intensity on the polymerization rate of MMA and DMAEMA.

The irradiation intensity has been changed by varying the distance between the lamp and the sample. The results are presented in Table 2. The relation between the polymerization rate and irradiation intensity is given by Eq.2:

$$R = C.I^n \qquad (2)$$

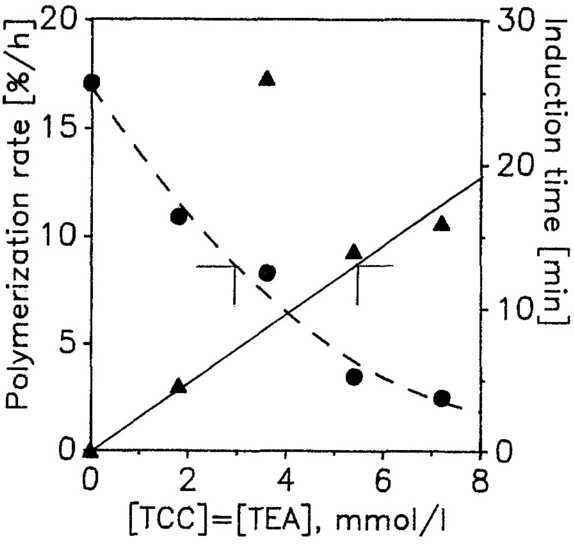

Fig.3. The influence of the inhibiting complex concentration on the induction time and polymerization rate of MMA.

Table 1. The effect of TCQ and TEA addition on the rate of photoinduced MMA and DMAEMA polymerization (the amount of TCQ and TEA is 50% of the initiator).

Composition	R_p [%/h] of	
	MMA	DMAEMA
Monomer alone	17	15
Monomer + TCQ	13	0
Monomer + TCQ*	-	6
Monomer + TEA	16	14

* The amount of TCQ is 6% mol of the initiator.

Table 2. The effect of irradiation intensity on MMA and DMAEMA polymerization rate.

Distance lamp-sample [cm]	R_p [%/h] of	
	MMA	DMAEMA
5	23	19
10	17	15
20	11	12
25	10	10
30	9	10

where C is a constant, I the light intensity and n is between 0.5 and 1 according to the polymerization mechanism (radical or ionic).

Our results provide a low n value (0.2-0.3) suggesting a complex polymerization mechanism and that initiation is probably a multi-stage process (1,2).

Conclusions

1. The inhibition of MMA and DMAEMA polymerizations by TCQ-tertial amine complexes is an evidence for the radical mechanism of these reactions.
2. The rate of DAI-photoinduced MMA and DMAEMA copolymerization is independent on the feed composition.
3. An abnormally weak photopolymerization rate dependence on the irradiation intensity is obtained, suggesting a complex initiation mechanism.
4. TCQ is not an efficient inhibitor of photoinduced MMA polymerization but its complex with TEA retards the polymerization after an induction period. In contrast, TCQ is a very strong inhibitor of DMAEMA polymerization because of monomer complexation.

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